Layer and size dependence of thermal conductivity in multilayer graphene nanoribbons

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Abstract

Using non-equilibrium molecular dynamics method(NEMD), we have found that the thermal conductivity of multilayer graphene nanoribbons monotonously decreases with the increase of the number of layers, such behavior can be attributed to the phonon resonance effect of out-of-plane phonon modes. The reduction of thermal conductivity is found to be proportional to the layer size, which is caused by the increase of phonon resonance. Our results are in agreement with recent experiment on dimensional evolution of thermal conductivity in few layer graphene.

Keywords: thermal conductivity, multilayer graphene nanoribbon, non-equilibrium molecular dynamics, size effect, phonon coupling

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The fresh comings of carbon family, the two-dimensional (2D) graphene and quasi-one-dimensional (1D) graphene nanoribbon (GNR), have attracted strong interest due to their fundamental physical properties and potential applications in nanoelectronic devices[1–4]. Experimental developments have enabled the growth of the high quality multilayer graphene[5] and the control of GNR edge geometries[6]. As we know, the thermal property is a crucial aspect that determines the application of a material in the nanoelectronics[7]. In recent years, the thermal properties of monolayer graphene and GNRs have aroused much attention [8–17]. Very recently, the thermal conductivity of few layer graphene has been also studied experimentally and theoretically[5]. However, the thermal conductivity of multilayer GNRs have not been well investigated so far. Its clarification is becoming desirable due to the forthcoming application of multilayer GNRs in nanoelectronics[18–20].

On the other hand, the mechanism of thermal conduction on the nanoscale is currently a controversial issue[7, 21]. Investigating the dimensional evolution of thermal conductivity could provide a new insight to clarify the fundamental mechanism on nanoscale. The thermal conductivity evolution from 2D to 3D had been investigated experimentally[5], while the evolution from 1D to higher dimensions is still not well studied. The multilayer GNRs are ideal systems for such investigation, whose dimensional evolution can be easily realized through the layer number and size variation.

In this letter, we employ the non-equilibrium molecular dynamics (NEMD) method to investigate layer and size effect on thermal conductivity of multilayer GNRs with different edge shapes, such as the armchair multilayer GNRs and the zigzag multilayer GNRs. The number of layers varies from 1 to 4 and the width of layers varies from 1 to 10 nm. We find that both the number of layers and size have strong influence on thermal conductivity of multilayer GNRs. The intrinsic mechanism of thermal conductivity variation is further explored through a phonon resonance model.

The structure of multilayer GNRs are constructed based on the theoretical prediction of bilayer GNRs which has a small deviation from Bernal stacking[22]. In the NEMD simulation, Tersoff potential[23] is utilized to describe the in-plane C-C bonding interactions and Lennard-Jones potential is used to describe the intra-plane van der Waals interactions[24]. We use the velocity Verlet method to integrate equations of motion with a fixed time step of 1 fs[17, 25–27]. On each layer of multilayer GNR**,** fixed boundary condition is implemented with the atoms at the left and right ends fixed at their equilibrium positions[16, 17]. Next to

the boundaries, the adjacent two cells of atoms are coupled to $Nosé - Hoover$ thermostats with temperatures 310 K and 290 K, respectively. The thermal conductivity for layer i can be calculated directly from the well known Fourier law $\kappa_i = J_i d/(\Delta T w h)$, where ΔT =20 K is the temperature difference between two thermostats, J_i is the heat flux from the heat bath to the system , which can be obtained via calculating the power of heat baths[25], d is the length, w is the width, h (0.144 nm)[17] is the thickness of a monolayer GNR. All the calculated thermal conductivities are obtained by averaging about 3 ns after 2 ns to establish a stable temperature gradient along the length direction. Thus the thermal conductivity of multilayer GNR can be defined as $\kappa = \sum \kappa_i/n$ with n being the number of layers. In addition, all the GNR structures have been optimized before NEMD simulation. We also define a multilayer GNR with N carbon-chains in width to be represented as *N*-armchair multilayer GNR or *N*-zigzag multilayer GNR, depending on the specific edge shapes[17].

We first investigate the number of layers dependence of thermal conductivity of 20-armchair multilayer GNR and 10-zigzag multilayer GNR. Similar to that of monolayer GNRs, the 20-armchair multilayer GNRs have much lower thermal conductivity than 10-zigzag multilayer GNRs (see Fig. 1), implying a universal edge-shape dependence of thermal conductivity in the GNR family. Moreover, with the number of layers increasing, thermal conductivity of both the armchair multilayer GNR and zigzag multilayer GNR monotonously decreases. When the number of layers gets to 4, the thermal conductivity is reduced to 123 $\mathrm{Wm^{-1}K^{-1}}$ and 308 $\mathrm{Wm^{-1}K^{-1}}$ for 20-armchair multilayer GNR and 10-zigzag multilayer GNR, respectively**.** Comparing with that of monolayer 20-armchair GNR (195 $\mathrm{Wm^{-1}K^{-1}}$) and 10-zigzag GNR (495 $\mathrm{Wm^{-1}K^{-1}}$), the reduction of thermal conductivity of armchair multilayer GNR and zigzag multilayer GNR gets to 40%, showing an obvious dependence on number of layers. This indicates that the crossplane coupling is enhanced with number of layers increasing, and it plays an important role in the evolution of thermal conductivity from monolayer GNR to multilayer GNR**.** This is in agreement with recent experiment in few layer graphene, where a 67% reduction of thermal conductivity is observed as the number of atomic plane increasing from 1 to 4[5].

These results can be further understood by the coupling mechanism[28], there exists a competitive mechanism on thermal conductivity in a coupling system: the phonon-resonance effect that decreasing thermal conductivity and phonon-band-up-shift effect that increasing thermal conductivity [28]. The strength of phonon resonance can be described by the res-

onance angle Ψ, which is determined by atomic mass and spring constant of two coupled systems. When Ψ is small($\Psi < \frac{\pi}{24}$), the variation of thermal conductivity is dominated by the phonon-band-up-shift effect; when Ψ comes to large($\Psi > \frac{\pi}{12}$), the thermal conductivity is dominated by the phonon resonance effect. The thermal conductivity reduction of multilayer GNRs with the increase of number of layers can be accounted for this mechanism. For the multilayer GNRs, the atomic mass and spring constant of the coupling layers are totally equivalent, thus $\Psi = \frac{\pi}{4}$ and the phonon-resonance effect plays a dominant role on thermal conductivity variation. Therefore, the thermal conductivity of multilayer GNRs monotonously decreases with the number of layers increasing which induces more and more intensive phonon resonance.

In order to identify the phonon-resonance effect in multilayer GNRs, we freeze the out-of-plane atomic vibration of multilayer GNRs and re-calculate their thermal conductivity. For simplicity, we consider the bilayer GNRs. Here we only present the calculated thermal conductivity values for the zigzag bilayer GNR, the results for armchair bilayer GNR are qualitatively similar. Two cases are considered: out-of-plane vibration of the top layer is frozen(constraint 1) and out-of-plane vibration of both layers is frozen(constraint 2).

As shown in Table 1, freezing out-of-plane atomic vibration would considerably change the layer's thermal conductivity. If only top layer's out-of-plane vibration is frozen, thermal conductivity of top layer would increase by 40% (from 334 $\mathrm{Wm^{-1}K^{-1}}$ to 467 $\mathrm{Wm^{-1}K^{-1}}$) while thermal conductivity of bottom layer is nearly unaffected by the artificial constraint. If the out-of-plane vibration is frozen in both layers, thermal conductivity of bilayer zigzag GNR almost equals to that of monolayer zigzag GNR. This indicates that, in the multilayer GNRs, the phonon resonance of stacking layers is mainly from the coupling between the crossplane out-of-plane ZO' phonon modes[29] and the out-of-plane phonon modes that propagate in the basal plane.

For the purpose of investigating finite size effect, we calculate thermal conductivity of both monolayer and bilayer GNRs with various width of GNRs. Figure 2 shows the obtained thermal conductivity of monolayer and bilayer GNRs, whose width ranges from 1 nm to 10 nm. As one can see, the thermal conductivity of zigzag bilayer GNR increases firstly and then turns to decrease with the width increasing, while the armchair bilayer GNR's thermal conductivity monotonously increases with the width increasing. The width dependence of thermal conductivity of bilayer GNRs is very similar to that of monolayer GNRs (Fig. 2).

This phenomena can be attributed to the competition between edge-localized phonon effect and the umklapp phonon scattering effect with the width of ribbon variation[17].

In addition, the difference of thermal conductivity between monolayer and bilayer GNRs also exhibits an obvious layer-size dependence. For the armchair GNRs (zigzag GNRs), the reduction of thermal conductivity monotonously increases from 31% (30%) to 35% (32%) with the width increasing from 1 nm to 10 nm. This means the difference of thermal conductivity between monolayer GNR and multilayer GNR is proportional to the layer size, because the phonon resonance strength between different layers is proportional to the number of total phonon modes which is in turn corresponding to the size of ribbon. Our results on thermal conducitivity reduction of multilayer GNRs is smaller than that of few layer graphenes[5]. Above results indicate that the difference in dimension evolution of thermal conductivity between multilayer graphene and multilayer GNRs comes from the finite size effect.

In conclusion, we have investigated the thermal conductivity of multilayer GNRs using the NEMD method. Comparing to monolayer GNR, the thermal conductivity of multilayer GNRs has a significant reduction which is in agreement with available experiments[5]. Based on the phonon resonance model, we propose that the reduction of thermal conductivity is attributed to the resonance of out-of-plane phonon modes. Moreover, the difference between thermal conductivities of GNRs with different number of layers is found to be proportional to the layer size, which is directly determined by the number of the total phonon modes. The present studies suggest that the thermal conductivity of multilayer GNRs can be manipulated by changing the number and size of layers, which provides potential applications of multilayer GNR-based materials in future nanodevices.

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Table I: Thermal conductivity κ of bilayer zigzag GNRs with different constraints. The length and width of the monolayer and bilayer zigzag GNR is about 10 nm and 3 nm.

Type of GNR	Constraint	Thermal Conductivity ($Wm^{-1}K^{-1}$)	
		Top Layer	Bottom layer
Bilayer zigzag GNR	Free	323	335
Bilayer zigzag GNR	Constraint 1	330	467
Bilayer zigzag GNR	Constraint 2	469	480
Monolayer zigzag GNR	Free	490	–

Constraint 1: Out-of-plane modes of top layer are frozen Constraint 2: Out-of-plane modes of both layers are frozen

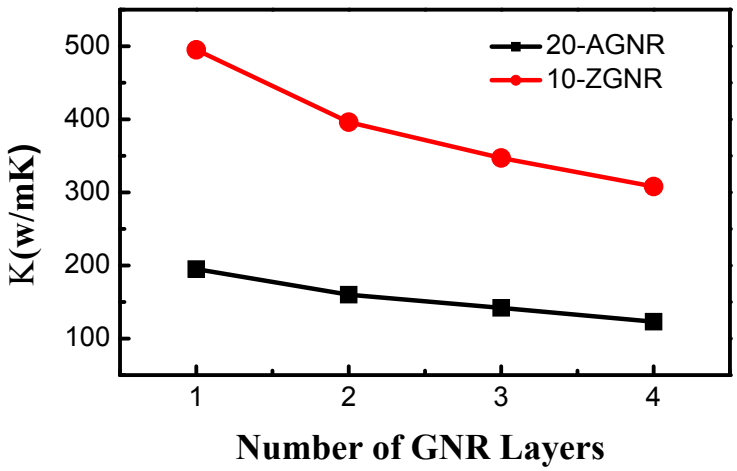

Figure 1: Thermal conductivity κ as a function of the number of layers with length and width of 5 nm and 2 nm. κ decreases monotonously with number of GNR layers increasing, indicating the enhancement of intra-layer phonon coupling.

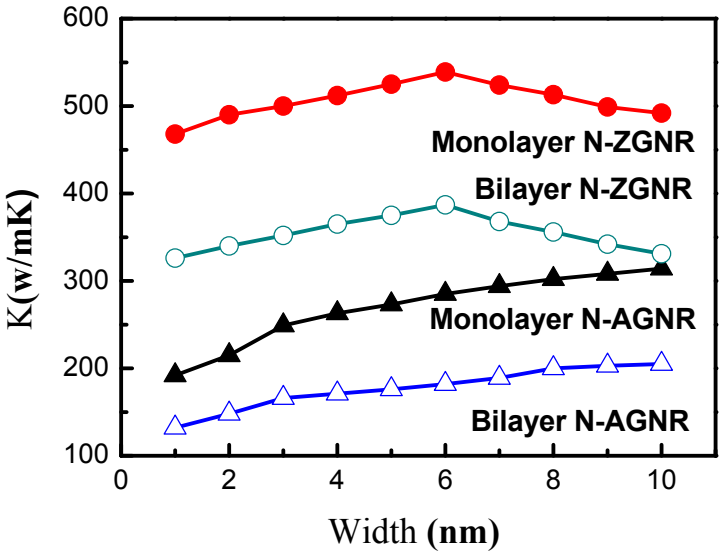

Figure 2: Thermal conductivity κ as a function of the width of monolayer or bilayer armchair GNR and zigzag GNR with fixed length of 10 nm. The behavior of κ for monolayer and bilayer is similar and the difference of κ between monolayer and bilayer GNRs increases with the width of GNRs increasing.